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(54) METHOD FOR MAKING MOLDING THERMOPLASTIC RESIN COMPOSITIONS

(71) We, JOTO CHEMICAL COMPANY, LTD., a Japanese Company of 15, Shodai-Tajika 3-chome, Hirakata-shi, Osaka-fu, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making a molding thermoplastic resin composition including a large amount of an organic or inorganic filler.

It is known that artificial stone products can be made by pressing with heat a mixture of a large amount of finely divided stones with the fluid prepolymer of a thermosetting resin, such as unsaturated polyester resin, epoxy resin or melamine resin, or heating and curing a similar mixture in which finely divided stones have been uniformly dispersed in the liquid prepolymer by, for example, shaking, or by pouring the fluid prepolymer into spaces between finely divided stones and then curing same. It is also known that artificial timber, or particle boards, can be produced by binding wood powders with a phenol resin.

In these conventional methods of preparing artificial stone and timber, it takes a great deal of time to cure the thermosetting resin by polymerization and also a lot of labor to pour the molding material into a metal mold and take out the molded objects. Moreover, what is worse in those methods, when the slightest mistake is committed in conditioning, the molding material tends to have air bubbles in it or crack, craze and shrink during curing, making it very difficult to produce standardized products.

Studies have been conducted on methods for the mass production of artificial stones and timber by using thermoplastic resins, instead of thermosetting resins, by means of an extruder but no satisfactory results have heretofore been obtained.

Since the thermoplastic resin material used for the purpose is generally in the form of powders or pellets, it would with difficulty be made sufficiently mixed and intimate with a large quantity of an organic or inorganic filler added by mere heat and pressure and any molding machine fed with such a composition often becomes unworkable. Or, even if it works, it can not give a product of superior quality. For example, if a mixture of polyethylene pellets with finely divided stones is put into a metal mold, pressed with heat and then cooled, there will be obtained a molded product of mediocre quality, and because of the poor intimacy of the resin with the filler material, the texture of the product would not be good enough. If finer pieces of broken rocks are employed, the degree of intimacy of the resin with the filler material would be somewhat improved, but there will still be unevenness in the permeation of the resin material into spaces between the pieces of rocks and there would not be obtained products having a fine texture, with the filler uniformly distributed. The same will be the case even when varied kinds of resin is used.

Further, when the molding composition is applied to an ordinary extruder whose cylinder and metal mold have been well heated, the machine would become overloaded and unworkable in a short time after start of operation due to the lack of lubricity of the filler and the insufficiency of melting of the resin. In order to overcome these defects, it has been proposed to mix and heat the resin pellets and the filler in a preheating vessel separately provided, and then feed them to the extruding machine. In this case, however, if the preheating temperature is no higher than the softening point of the resin itself, the extruding machine would, similarly to the above case, become overloaded. On the other hand, if the preheating temperature is made as high as about the melting point of the resin, the resin pellets will become fused with each

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other by the slightest mixing movements in the pre-heating vessel, and it would become difficult for the material to be poured into the extruder; if poured by force, the molding material tends to adhere closely to the screw between the feeding and compression zones, leaving the machine running idle. Only when the pre-heating temperature is made a little higher than the softening point of the resin, will the extruder remain workable for some time, but thereafter the amounts being extruded become gradually smaller, until at last the resin is fused to the screw, making the operation of the extruding machine entirely impossible. Thus, no satisfactory results may be given in any of the cases.

There is therefore a need to provide a molding method which makes it possible for a molding machine, such as an extruding or injection-molding machine, to be operated continuously, even when large amounts of filler are used for mixing with the thermoplastic resin, and more particularly a method for continuously producing artificial stones and timber in large quantities at low costs by employing a variety of molding machines, such as extruders, injection-molding machines, and calendar rolls attached to and cooperative with kneading rolls.

The present invention provides a method of making a molding thermoplastic resin composition which comprises mixing a thermoplastic resin with a filler, at a true volume ratio in the range 1 to 0.5 to 1 to 1.5, the filler being preheated to a temperature at which the filler will have an amount of heat sufficient for heating the resin ingredient to its melting point and which is 50° to 200° higher than the melting point of the thermoplastic resin, and subsequently kneading the resultant mixture under pressure.

The resin will normally be in the form of a powder or pellets. The filler may be organic or inorganic.

To give a more detailed description of the invention, the preferred resins employed are selected from the group consisting of polystyrene, polyethylene, polypropylene, polyvinyl chloride, polyamide, AS resins, ABS resins, and other thermoplastic resins, having a comparatively high thermal stability and a low viscosity when molten, although the invention is not limited thereto.

The organic fillers are exemplified by various wood splinters usually in the size of from 1 mm to 10 μ , such as sawdust, although not limited thereto. It is preferable that water content in the filler is no more than 10%, so that the generation of air bubbles may be prevented while the filler is kneaded with the resin. The inorganic fillers are exemplified by stone, granite, andesite, and other stones, all finely divided, and calcium carbonate, silica, clay, asbestos, gypsum, alumina, cement, and glass, in the form of granules or powder.

In practicing the method of the invention, other additives such as coloring agents or stabilizers may be employed, if necessary. Especially when an organic filler is used, it may be treated with a suitable dispersing agent or a lubricant, such as a surface active agent, wax, lead stearate or a thermosetting resin, for example, an epoxy resin or an unsaturated polyester resin, in order to improve the intimacy of the filler with the thermoplastic resin.

The gist of the present invention lies in preheating the inorganic filler to a temperature at which the filler will have an amount of heat sufficient for heating the resin ingredient to its melting point and, at the same time, about 50° to 200°C higher than the melting point of the resin prior to mixing, and then shifting the mixture of resin and filler to the compression-kneading process. Here, there is established the following relation between the temperature of the thermoplastic resin and the temperature to which the filler is preheated:

$$W_1 C_1 (T_m - T_1) = W_2 C_2 (T_2 - T_m)$$

where W_1 and W_2 are the weight of the resin and the filler, respectively, C_1 and C_2 are the specific heat of the resin and the filler, respectively, T_1 and T_2 are the temperature of the resin and the preheated filler, respectively, and T_m is the melting point of the resin.

In the above-mentioned equation, the preheat temperature of the filler, T_2 , is equivalent to the amount of heat in the filler which is required to heat the resin up to its (the resin's) melting point. In other words, T_2 is understood to be a minimum temperature to which the filler should be preheated, because the filler-resin molding composition is usually kneaded at a temperature somewhat higher than the melting point of the resin, say, by 50 to 100°C or more, and in order to cause the resin to be heated to above its melting point, the filler is required to have been preheated to a temperature higher than the value of T_2 in the equation. For the accomplishment of the invention, it is necessary to determine the preheat temperature of the filler at a temperature such that the amount of heat carried by the preheated filler is enough for heating the resin to above its melting point, such temperature always being higher than the value of T_2 in the equation.

Further, it has been discovered that undesirable results can be obtained when the preheat temperature of filler is in the range of from 50° to 200°C higher than the melting point of the resin. When the preheat temperature of the filler is under the lower limit, the resin would not be sufficiently molten. On the other hand, when it is above the higher limit, there is a possibility of causing deterioration of the resin. The most suitable preheat

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temperature of the filler depends upon the kind of the filler and the resin used and also upon their mixing ratios; however, it can be determined based on the above mentioned equation by a person skilled in the art.

The value of the T_M is presumed in consideration of the compression-kneading condition and not the proper melting of the resin. For example, where an extruder is employed, the T_M represents an estimated melting point in the early period of the compression-kneading process. On the other hand, W_1 , C_1 , W_2 and C_2 are determined values, depending on the kind of resins and fillers. As such, once the T_1 is determined, the T_2 can be easily known by means of the equation given above. It follows, therefore, the value of T_2 is about 50 to 200°C higher than that of T_1 . It should be noted in practicing the method of the invention that the T_2 value must not be lower than the melting point of the resin, and the mixing ratio by true volume of the resin to filler must be such that the temperature due to the heat given to the resin by the filler will be lower than the decomposition point of the resin. In particular, when there is employed an organic filler, for example, wood powders of 1 mm to 10 μ sized, it should be taken into consideration in determining the T_1 and T_2 that the filler tends to become carbonized at 200°C or above. As is clear from the equation, it is advisable, though not always required, to preheat the thermoplastic resin to around its softening point in order to effectively utilize the heat of the filler.

It is proposed that the ratio by true volume of the thermoplastic resin to the filler to be mixed with each other varies between 1:0.5 and 1:1.5, because if the volume of the filler is below 50% of that of the resin, the artificial stone or timber made from such a composition would not possess desirable properties, and if it exceeds 150%, the molten resin would not become intimate with the filler, and the moldability of the compression-kneaded mixture would deteriorate.

Desirably the resin ingredient constitutes at least 25 per cent by weight of the product.

Now, for the purpose of bringing about a better understanding of the invention, the mode of an embodiment by means of an extruder machine will be given below.

Certain resin pellets and fillers are preheated under the conditions described above and lightly mixed with each other before they are fed to an extruder. The preheated fillers melt the surfaces of the resin pellets which have been somewhat softened, so that each pellet is entirely covered with some of the fillers. The filler-covered pellets, then mixed with the remaining filler, are supplied to the feed zone of the extruder. The composition thus fed then proceeds to the compression zone, with only the filler itself coming in contact with the surfaces of the machine parts.

At the compression zone, the filler components penetrate into the resin pellets and as the heat of the filler spreads to the resin components, the whole composition is converted all at once into the state of melt, and well kneaded. The composition then enters into the melting zone and becomes to be a uniform melt, which is extruded from the die. In the process, the cylinder should be heated only at the beginning of the operation of the machine, for during the later operation, the heat given by the filler itself and the frictional heat caused by mixing the filler with the resin will be enough. The surfaces of the cylinder may be kept cool by means of a fan or the like. Under such condition, there can be no sticking of the resin to the surfaces of the screw, or no reduction in quantities of the composition extruded. Further, when the heat given by the organic filler is less than that given by the inorganic filler, the cylinder may be heated as occasion demands.

To explain the circumstances, speaking of the three temperatures, viz., the temperature of the screw, that of the resin, and that of the cylinder, the first is highest in the part other than the feed zone, and the third lowest. The screw temperature is higher than the others since it is imparted by the preheated filler and the frictional heat, and there is also little heat escape from the screw itself. It is generally said that resins are apt to adhere to highly heated metals, but this is true only when the metal surfaces coming in contact with the resin is considered. Factually, the resin in contact with highly heated metals is of low viscosity, while that coming in contact with slightly heated metals is of high viscosity. Consequently, when the revolving or shearing power is working, the surface of the screw has a low frictional resistance, and that of the cylinder has a high frictional resistance, giving an ideal condition under which a sufficient propulsion is given to the mixture.

The method of the present invention is applicable not only to extruders but also to other molding machines.

Taking kneaders for example, the prescribed amounts of a resin and a filler, having been heated to T_1 and T_2 , respectively, with T_M a little higher than in the case of an extruder, were fed to one which had been preheated a little higher than T_M , and there was obtained a uniform melt in a short time. Under different preheating conditions, however, the resin alone adhered to the walls of the heated instrument, failing to give a uniform mixture, although it took a longer time to complete the process.

Further, as another example, a roll was employed with the resin and filler which had been treated under conditions similar to the case of the above kneader before being lightly mixed so that each resin pellet was covered with the filler. In this example, the first step

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of operation of roll-kneading could be completed in a short time, where the resin came to adhere to the surfaces of rolls only after having absorbed the heat of the filler and mixed-melt to a considerable extent.

The molded products prepared from compositions of a thermoplastic resin and an organic filler, such as wood powder according to the method of the present invention, proved to have strength as high as that of ordinary timber. They are able to be sawn, screwed and nailed, just as is done with natural timber. They are quite different for technical reasons from ordinary synthetic timber which is a product of high density foams from thermoplastic resins.

A variety of molded objects can be made by the method of the invention from thermoplastic in combination with an inorganic filler instead of an organic one. For example, products from the combination of polyethylene and lime stone are useful for marble-like floor panels (boards); those from polystyrene and lime stone are used as hard artificial stone products for making walls and furniture. Another example is products from polypropylene and calcium carbonate, which are recommended as boards having appropriate rigidity and flexibility.

Next, the invention will be more fully described but not limited by the following examples in which conditions and procedures of molding are given.

Example 1.

A. Molding conditions:

(1) Composition:

Resin I: Blown high-pressure polyethylene, finely divided (containing some pigments).
100 parts by weight.
True specific gravity: 0.95.

Filler I: Sawdust from cedar wood,
100 parts by weight.
True specific gravity: 0.80.
(Volume ratio of Resin I to Filler I:
About 1:1.2).

(2) Preheating temperatures:

Resin I : 90°C.
Filler I : 160°C.

(3) Specification of extruding machine employed:

Diameter of the cylinder : 70 mm
L/D of the cylinder : 20 mm
Compression ratio : 1:2.2

Cylinder: On the inside walls of the feed zone are cut vertical grooves in order to strengthen the propulsion which the machine gives to the composition fed to it.

Temperatures:

Feed zone : 130°C
Compression zone : 170°C
Melting zone : 170°C
Die : 200°C
(The screw is equipped with a heater.)

Extruding die:

Having a rectangular outlet, 150 mm wide and 20 mm high.

B. Molding procedure:

Resin I and filler I, preheated at temperatures as given in (2) above were lightly tumbled and fed to the preheated hopper of the extruding machine, and the machine was set working. In about 5 minutes, through the metal mold at the outlet of the extruding machine was extruded a board of uniform resin composition, 20 mm thick and 150 mm wide, equal to the outlet of the die. The board was then compressed with a heated calendar to be gradually cooled. In this way an artificial timber of uniform texture with a smooth surface was continuously obtained.

Example 2.

A. Molding conditions:

(1) Composition:

Resin II: Blown polystyrene, finely divided.
100 parts by weight.
True specific gravity : 1.05.

Filler II: Finely divider chips of splint.
80 parts by weight.
True specific gravity : 0.8.

(2) Preheating temperatures:

Resin II : 100°C
Filler II : 150°C

(3) Specification of kneading roll employed:

Diameter : 300 mm
Temperatures: 160°C at the front roller
150°C at the rear roller

Rolling ratio of the front roller to the rear: 1:1.3

B. Molding procedure:

Resin II and filler II were lightly tumbled, and fed to the roll. First the crevice between the two rollers was kept as narrow as 2 mm, and the composition fed to the roll was received on the receptacle. After the composition was fed to the roll twice or so, it would be completely rolled on the rollers. Then the crevice of the rollers was widened to about 5 mm, and by recharging the composition several times, there was obtained a resin com-

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	position of uniform texture, which was put, in one lot, into a metal mold preheated to about 170°C, then pressed with a press and immediately cooled. The product obtained was tough and shaped as desired, with attractive surfaces and fine texture.		
	Example 3.		
	A. Molding conditions:		
	(1) Composition:		
10	Resin III: Low pressure polyethylene pellets.		
	100 parts by weight.		
	Specific gravity : 0.95.		
	Specific heat : 0.55.		
15	(Softening point : 120°C.)		
	Filler III: Finely divided lime stone (Average diameter : 0.5 mm).		
	200 parts by weight.		
	Specific gravity : 2.7.		
20	Specific heat : 0.2.		
	(2) Preheating temperatures:		
	Resin III : 90°C.		
	Filler III : About 190°C.		
	(3) Specification of extruder employed:		
25	Diameter of the cylinder : 70 mm		
	L/D of the cylinder : 20 mm		
	Compression ratio : 1:1.7		
	Temperatures:		
	Feed zone : 140°C		
30	Compression zone : 160°C		
	Melting zone : 170°C		
	Die : 180°C		
	Extruding die:		
35	having a rectangular outlet, 150 mm wide and 5 mm high.		
	B. Molding procedure:		
	The extruder was operated at 20 rpm, and a melt was obtained through the metal mold 3 minutes after the start of the operation.		
40	Then, the melt became a uniform mixture and stable operation of the molding machine could be continued for 10 minutes or so. During the operation, the temperatures at the compression and melting zones were lowered		
45	to 150°C and 160°C, respectively, and cooling with a fan was repeated. The rpm of the machine was increased to 28, and the current from the motor was kept at 22 A. A melt of uniform quality was extruded at the rate of 1		
50	kg per minute, or 60 kg per hour. When the melt was cooled as it went through a calender, there was obtained an artificial stone with smooth surfaces, having proper rigidity and flexibility.		
	Example 4.		55
	A. Molding conditions:		
	(1) Composition:		
	Resin IV: Styrene resin GP pellets.		
	100 parts by weight.		
	Specific gravity : 1.05.		60
	Specific heat : 0.4.		
	(Softening point : 100°C)		
	Filler IV: Finely divided lime stone		
	Average diameter : 0.5 mm)		
	300 parts by weight.		65
	Specific gravity : 2.7.		
	Specific heat : 0.2.		
	(2) Preheating temperatures:		
	Resin IV : 110°C.		
	Filler IV : About 193°C.		70
	(3) Kneader employed:		
	1 Hp. Heated to 170°C with an oil heating jacket.		
	B. Molding procedure:		
	Resin IV and filler IV were heated in separate vessels, then taken out and put into a metallic vessel. After they were tumbled lightly in the vessel with a lid on, the whole mixture was fed to a revolving kneader. In about two minutes, a melt of uniform texture was obtained. Then, some of the melt was put into a metallic vessel, preheated to 150°C and immediately cooled under pressure to obtain an attractive artificial stone having high hardness.		75
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			85
	WHAT WE CLAIM IS:—		
	1. A method of making a molding thermoplastic resin composition which comprises mixing a thermoplastic resin with a filler, at a true volume ratio in the range 1 to 0.5 to 1		90
	to 1.5, the filler being preheated to a temperature at which the filler will have an amount of heat sufficient for heating the resin ingredient to its melting point and which is 50° to 200° higher than the melting point of the thermoplastic resin, and subsequently kneading the resultant mixture under pressure.		95
	2. The method of claim 1 wherein said filler is an organic substance in powder or granular form.		100
	3. The method of claim 1, wherein said filler is wood powder and the kneading is effected with an extruder or a kneader roll.		
	4. The method of claim 1 wherein said filler is an inorganic substance in powder or granular form.		105
	5. The method of claim 1, 2 or 3 wherein		

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said thermoplastic resin is preheated to about its softening point.

6. The method of claim 4 wherein said thermoplastic resin is preheated to about its softening point.

7. The method of claim 1 substantially as hereinbefore described in any of the Examples.

8. A molding composition made by the method of any preceding claim.

9. A moulded product made from a composition according to claim 8.

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